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Molecular bottle brushes in thin films: An off-lattice Monte Carlo study

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The effect of intramolecular excluded volume interactions on the conformations of isolated comb-shaped copolymers—''molecular bottle brushes''—in athermal solvents confined between two hard impenetrable parallel plates is studied by off-lattice Monte Carlo simulations. Equilibrium conformational properties of molecules consisting of a freely jointed backbone of 100 hard spheres (beads), where 50 equally flexible side chains of lengths M up to 30 beads are connected, are determined as a function of the width of the slit, including the pure two-dimensional (2D) case. Besides general properties such as the size and the shape of the chains and the orientation of the chains with respect to the confining plates, the persistence length of the bottle-brush backbone λ is considered in particular. It is demonstrated that due to the side chains, the backbone is, in fact, effectively confined between two *soft* plates, i.e., the side chains act like softening springs between the backbone and plates. The most striking result is that, unlike the three-dimensional (3D) situation, in the 2D case the ratio between λ and the diameter D, λ/D, of the bottle brush starts to increase as a function of the side chain length for $M \geqslant 10$. For 3D, an increase of λ/D (the essential parameter for lyotropic behavior) as a function of M is predicted by theory but has so far not been observed numerically for the regime studied (i.e., $M \leqslant 30$). These results suggest that due to the weaker excluded volume effect in 3D, a possible upturn of λ/D may only be observed for longer side chains than studied so far. © *1999 American Institute of Physics.*
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I. INTRODUCTION

To control the conformation of polymer molecules is one of the central issues in polymer science. It is well known that an isolated flexible polymer chain typically adopts a coiled conformation when dissolved in a solvent. There are, however, different methods to adjust the coil size and extension of the chains. For example, in aqueous solutions, it is even possible to obtain rodlike structures by using strong electrostatic interactions between chain segments.[1,2] The stiffness of such polyelectrolytes, defined by the persistence length λ, can be controlled, for example, by the concentration of salt added.

In noncharged polymer solutions one can ask whether the intramolecular excluded volume interactions between the different polymer segments suffice to yield extended chain conformations even for flexible polymers, provided more complex polymer architectures such as comb copolymers are used. Furthermore, if stiffening is obtained, can it be to such an extent that lyotropic behavior becomes possible. In recent years these issues have been discussed extensively with respect to ''molecular bottle brushes'' consisting of a flexible backbone and relatively long flexible side branches spaced densely along the backbone. These comb-shaped copolymers have been studied experimentally,[3–8] theoretically,[9–11] and by computer simulations[11–17] (for a recent review see Ref. 18).

According to Fredrickson,[9] the aspect ratio λ/D of the bottle brush dissolved in a good solvent (where D is the diameter of the bottle brush) increases as a function of the side chain length M ($\lambda/D \propto M^{9/8}$), provided of course that the lengths of the backbone and side chains are sufficiently large to validate the scaling approach employed. Therefore, by selecting long enough side chains, it should be possible to obtain $\lambda/D > 10$, thereby satisfying the condition for nematic lyotropic behavior of semiflexible chain molecules.[19,20] However, the opposite view was expressed by Birshtein and co-workers,[10] who came to the conclusion that the persistence length of the backbone and the diameter increase in the same way as a function of the length of the side chains, implying that λ/D remains constant ($\lambda/D \propto M^0$). Because of these conflicting theories, and also because of the scientific importance, we decided some time ago to study computationally molecular bottle brushes in some detail.[13,14] It was demonstrated[13] that in the three-dimensional (3D) case the flexible backbone of a bottle brush indeed extends considerably due to the excluded volume interactions between the side chains. However, no indications of an increase in the ratio λ/D as a function of the side chain length was found; rather a slight decrease of this ratio was observed. In our

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most recent paper[14] we also considered side chains consisting of beads which are larger than those of the backbone. The corresponding increase in the intramolecular excluded volume interactions led to a larger persistence length. Moreover, the ratio λ/D increased strongly as a function of the size of the side chain beads, however, it remained, as before, approximately constant as a function of side chain length.[14]

At this point, there appear to be two possibilities. Either the Birshtein *et al.* conclusion, $\lambda/D \propto M^0$, is correct, implying that the Fredrickson prediction, $\lambda/D \propto M^{9/8}$, is wrong or the size of the bottle brushes is still too small, i.e., we are still far outside the scaling regime where these scaling relations are supposed to hold. We will address this issue here, not by studying much larger structures but rather by considering a situation in which the excluded volume effect is much larger and known to be already more effective for smaller chain lengths, i.e. the two-dimensional (2D) situation.

Recent experiments provide additional motivation to study molecular bottle brushes in thin film.[7,8] Molecular bottle brushes, consisting of poly(2-vinylpyridine) (P2VP) side chains, were experimentally characterized by Möller and co-workers[7] using atomic force microscopy (AFM), for example. They managed to visualize strongly extended conformations of single molecules by using a highly diluted solution of bottle brushes in chloroform (a good solvent for P2VP) sprayed onto mica. As pointed out by the authors,[7] since mica has a strong interaction with P2VP, the molecules were effectively ''squeezed'' on the surface. This also shows that it is of considerable interest to study computationally the influence of confinement on the conformations of molecular bottle brushes.

Finally, recent computational[21–23] and theoretical[24] results for isolated linear chain molecules confined between two parallel plates demonstrate that the crossover from 3D to 2D is highly nontrivial. As an example, it was shown that the radius of gyration, rather than monotonically increasing as a function of decreasing distance between the confining plates, adopts a minimum at a characteristic distance. Molecular bottle brushes have a much more complex architecture, involving the backbone and the side chains as separate entities, and it is clearly of interest to see how this is reflected in the crossover behavior.

II. MODEL AND DETAILS OF THE SIMULATION

Off-lattice Monte Carlo (MC) simulations were performed to study the equilibrium conformations of molecular bottle brushes confined between two parallel hard plates. The focus is on the behavior of a single isolated molecule in a good athermal solvent. The molecules were modeled as freely jointed chains of hard spheres (beads) consisting of a backbone of 100 beads of which every second, i.e., 50, carry a side chain of a given length M varying from 0 [corresponding to a simple coil obeying self-avoiding walk statistics (SAW)] to 30. All the beads of the system, irrespective of whether they belong to the backbone or to the side chains, have the same size. It is important to realize that for the given backbone size, not much longer side chains can be used. Due to the chain end effects, we would enter into the star rather than bottle-brush polymer regime. The diameter of the beads is taken to be equal to the length of the bond between neighboring beads and it is taken as the unit length for all the geometrical dimensions of our simulations. The separation between the hard plates, ΔZ, placed perpendicular to the z axis, was varied between 1.0 (2D case) and infinity (3D case), focusing mainly on lateral distances comparable with the size of the molecule. Since there are only excluded volume interactions, the potential energy between any two beads i and j has the form

$$U_{ij} = \begin{cases} 0 & \text{if } i \text{ and } j \text{ are neighbors or } |\mathbf{r}_{ij}| > 1, \\ \infty & \text{otherwise,} \end{cases} \tag{1}$$

where $\mathbf{r}_{ij}$ is the vector connecting beads i and j. Furthermore, the potential energy between bead i and the plates is given by

$$U_{i,\text{plates}} = \begin{cases} 0 & \text{if } |r_{i,z}| < \dfrac{\Delta Z - 1}{2}, \\ \infty & \text{otherwise,} \end{cases} \tag{2}$$

where $r_{i,z}$ is the z coordinate of the position of bead i. Consequently, the total energy of the system can be written as

$$U = \sum_{i<j} U_{ij} + \sum_i U_{i,\text{plates}}. \tag{3}$$

Configuration space is sampled according to the Metropolis importance-sampling scheme.[25] The trial moves consist of different types of local chain rotations introduced in our previous papers.[13,14] Additionally, we used more global pivot-type[26] rotations and center-of-mass motions to get faster statistically uncorrelated conformations. Although the acceptance ratio of the pivot steps in our densely grafted structures is quite small, especially for structures with long side chains, the speed up was found to be remarkable. The reason is that once a pivot step is accepted, we end up with globally new conformations. The same fact was recently emphasized by Rouault,[12] using a lattice model to study long comb copolymers, however, with much lower grafting densities. It is important to realize that the used simulation method allows redistribution of the side chains irrespectively of the width of the slit and, therefore, even in the ''pure'' 2D case we are dealing with annealed rather than quenched averages.

The initial conformations were formed as 2D structures in the xy plane. The hard plates were placed perpendicular to the z axis. All simulations were divided into 11 blocks and the first block was used only to equilibrate the bottle brushes. The number and optimal combination of different types of MC steps used per simulation block depend strongly on the particular structure and separation between the plates. To give an example, for the structures having side chains of length 20, between 1000 and 24 000 MC steps per simulation block were needed. About 75% of the attempted steps of backbone beads were local rotations while 25% were pivot-type ''bendings'' of the whole end part of the molecule. For side chains, about half of the steps were local and half consisted of pivot-type bending of the end part of the given side

chains. For the above-mentioned structure, a MC step corresponds to 1100 (total number of beads of the molecule) attempted steps.

For all the remaining ten actual simulation blocks the average values of the quantities of interest were computed using at least 100 conformations taken from the simulation block at equally spaced intervals. Finally, the average of the block averages was calculated and the errors were estimated with 95% confidence intervals using the standard deviation of the block averages.

III. RESULTS AND DISCUSSION

In this section, we present the results of our off-lattice Monte Carlo simulations of isolated molecular bottle brushes, consisting of a backbone of 100 beads and 50 side chains of lengths up to 30 beads, confined between two hard parallel plates in good athermal solvent. We first consider the changes in the conformations of the structures with a fixed side chain length during the crossover from the free 3D case to the 2D case by squeezing the molecules between the plates. Then, we consider the behavior as a function of the side chain length M, concentrating on the difference between the 3D and 2D situation.

A. Squeezing of a bottle brush between two impenetrable parallel plates

We focus first on the behavior of the bottle brushes with side chains of length $M=16$. However, qualitatively the same behavior was observed for all the other structures ($M=6$, 12, and 20) studied as a function of the separation between plates ΔZ. Figure 1 shows typical conformations of the molecule consisting of a backbone of 100 beads and 50 side chains of length 16 for different separations between the plates. Figure 1 illustrates in a striking manner how the molecular bottle brushes become much more extended, due to the increased intramolecular excluded volume effect, as the separation between the plates decreases.

A more quantitative measure of this behavior is given in Fig. 2, which shows the root-mean-square end-to-end distance R_e of the bottle-brush backbone and the persistence length λ of the backbone as a function of ΔZ. The persistence length was estimated using the bond-angle correlations of the backbone segments. In principle, the relation between the persistence length and the bond-angle correlations is given by

$$\langle \cos\ \theta(s)\rangle = e^{-s/\lambda}, \tag{4}$$

where $\langle \cos\theta(s)\rangle$ is the average cosine of the angle between two chain segments separated by a length s along the chain. However, as previously demonstrated,[13,14] the correct description of the bottle-brush backbone requires at least two characteristic lengths, one describing the short length flexibility and the second describing the long distance stiffness of the backbone. Since we are obviously interested in the latter, the middle linear part of the correlation data (we selected $5<s<50$) was used to calculate the persistence lengths (see Fig. 3). These figures refer to backbone conformational properties. To characterize the behavior of the side chains during squeezing, Fig. 4 presents the root-mean-square end-to-end distance R_e of the side chains as a function of ΔZ.

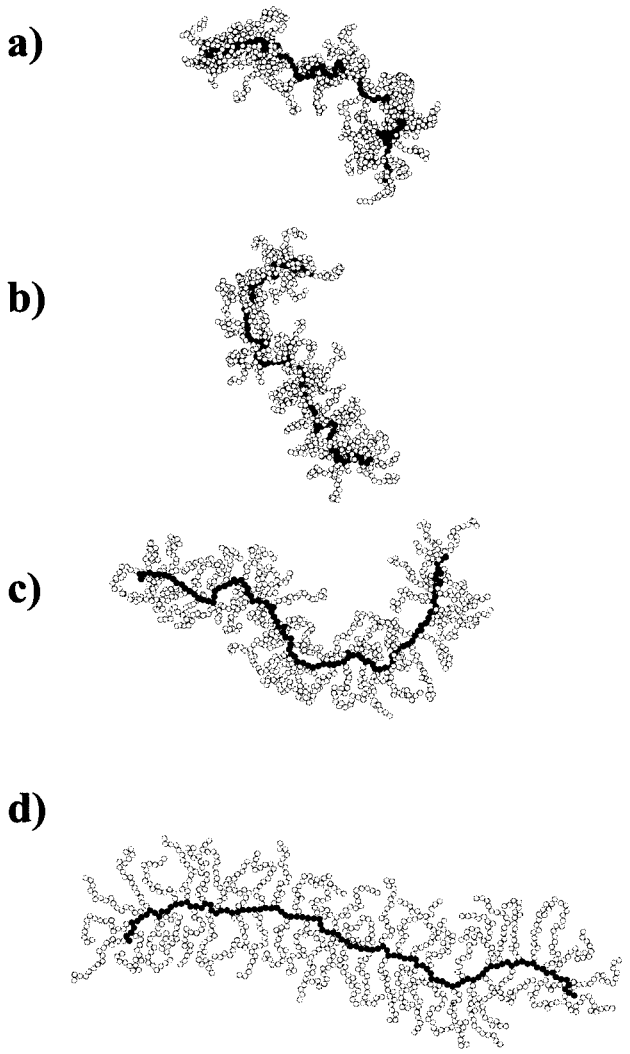

FIG. 1. Characteristic conformations of a molecular bottle brush confined between two parallel plates separated by a distance ΔZ. (a) $\Delta Z=\infty$ (3D case); (b) $\Delta Z=17$; (c) $\Delta Z=5$; and (d) $\Delta Z=1$ (2D case). The structures are snapshots from the simulations of the molecule consisting of a backbone (black) of 100 beads and 50 side chains (white) of 16 beads each. The view is from the direction of the smallest eigenvector of the radius of gyration tensor of the molecule.

Several conclusions can be drawn. Both the backbone and the side chains start to extend due to the squeezing: the backbone at around $\Delta Z=40$ and the side chains at $\Delta Z=10$. However, the striking difference between the two cases is that R_e of the side chains has a clear minimum whereas R_e of the backbone increases quite monotonically where the persistence length has only a very flat, if any, minimum. Consequently, the side chains seem to behave in the ''conventional'' way. As shown both by theory[24] and by simulations,[21,22] isolated linear chains confined between two hard parallel plates behave qualitatively in the same manner as the side chains. During squeezing of linear chains, the molecules first orient with the two longest principal radii of gyration parallel to the plates. Further squeezing first deforms the coils slightly, thereby reducing the end-to-end distance as well as the radius of gyration. Upon still further

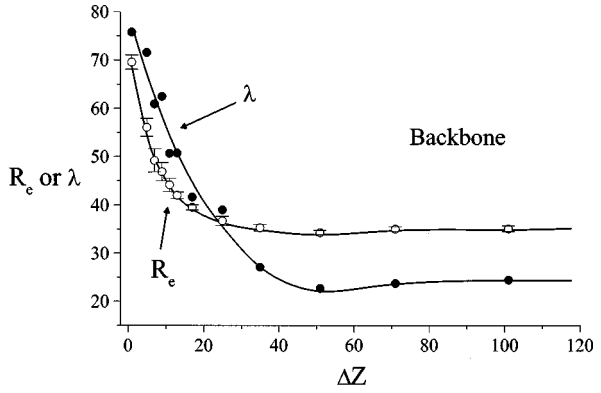

FIG. 2. Root-mean-square end-to-end distance (○) R_e and persistence length (●) λ of the bottle-brush backbone as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

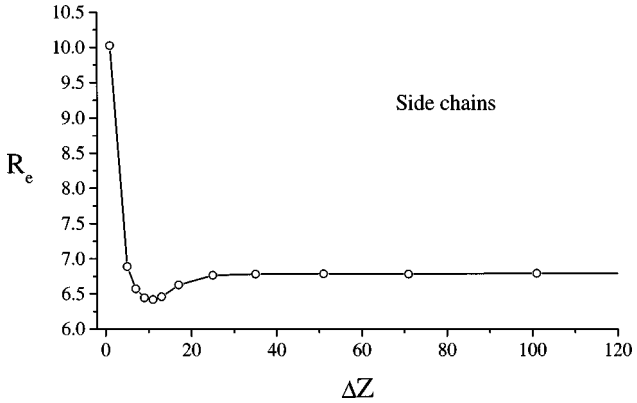

FIG. 4. Root-mean-square end-to-end distance R_e of the side chains of length 16 as a function of the separation between the confining plates ΔZ.

squeezing, the increase in excluded volume interaction takes over and both quantities increase towards their 2D value. The fact that for the bottle brushes the backbone only shows a shallow minimum at best, follows from the fact that side chains screen the hard plates so that the backbone, the beads of which are mainly located in the middle of the slit, effectively feels two *soft* plates. According to recent theories soft plates really make the minimum flat.[24]

The discussion about possible lyotropic behavior of molecular bottle brushes centers around the question of whether the ratio between the persistence length and the bottle-brush diameter is large enough (>10).[19,20] To address this issue, the bottle-brush diameter D will be defined as twice the root-mean-square end-to-end distance of the side chains ($D=2\times R_e$). Using the persistence length λ of the backbone also for the bottle brush, this results in the behavior of λ/D as shown for $M=16$ in Fig. 5. The most striking observation is that λ/D increases considerably when the separation between the plates is decreased. Moreover, due to the minimum of the root-mean-square end-to-end distance of the side chains (Fig. 4), this ratio has a maximum at a characteristic value of ΔZ, after which further squeezing decreases the ratio towards its final 2D value. The above-mentioned results agree well with the recent experimental observations of Möller and co-workers,[7] where molecular bottle brushes were characterized using AFM. Since the samples were prepared by spraying the molecules onto the strongly interacting surface of mica, the molecules are effectively confined between two plates leading to strongly extended structures.

To characterize the conformational behavior in more detail, we will consider the radius of gyration tensor[27] T, which is defined by

$$T_{\alpha\beta}=\frac{1}{N}\sum_{i=1}^{N}(r_{i,\alpha}-r_{\mathrm{cm},\alpha})(r_{i,\beta}-r_{\mathrm{cm},\beta}), \tag{5}$$

where α and β refer to the x, y, and z components of the position of the beads of the studied chain ($r_{i,\alpha}$) and the center of mass of the chain ($r_{\mathrm{cm},\alpha}$). The eigenvalues of T, denoted in the descending order as λ_1, λ_2, are λ_3, are called the principal radii of gyration and they may be considered as the squared lengths of the principal axes, given by the corresponding eigenvectors, of an ellipsoid describing the shape of the structure. Figures 6–11 show the average eigenvalues of the backbone and side chains as a function of ΔZ for molecules with 100 backbone beads and 50 side chains with 16 beads each. To see the orientation of the corresponding principal axes with respect to the plates, the same figures

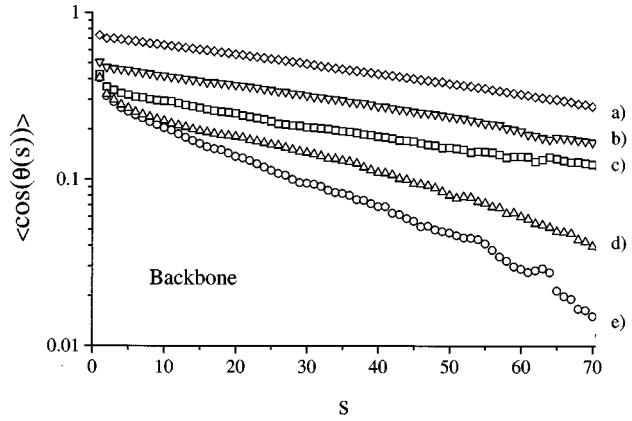

FIG. 3. Bond-angle correlations $\langle\cos[\theta(s)]\rangle$ as a function of the separation s along the backbone for the bottle brushes consisting of a backbone of 100 beads and 50 side chains of length 16. (a) $\Delta Z=1$ (2D case); (b) $\Delta Z=5$; (c) $\Delta Z=9$; (d) $\Delta Z=17$; and (e) $\Delta Z=\infty$ (3D case).

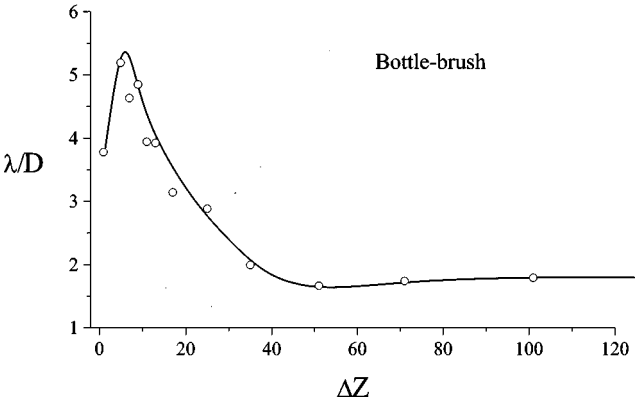

FIG. 5. The ratio of the persistence length λ and the bottle-brush diameter D as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

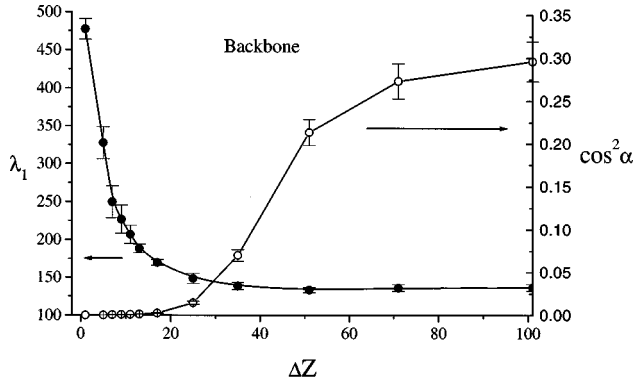

FIG. 6. The largest eigenvalue (●) λ_1 of the backbone and the orientation function of the corresponding eigenvector (○) $\cos^2\alpha$ as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

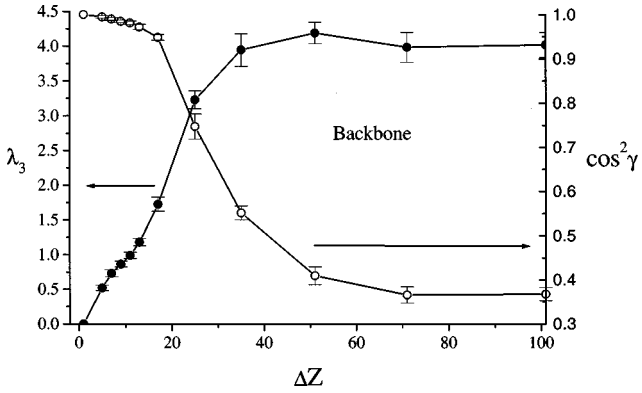

FIG. 8. The smallest eigenvalue (●) λ_3 of the backbone and the orientation function of the corresponding eigenvector (○) $\cos^2\gamma$ as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

also include the orientation functions, $\cos^2\alpha$, $\cos^2\beta$, $\cos^2\gamma$, giving the square cosines of the angles between the eigenvectors of the radius of gyration tensor and the z axis. Note that in the case of parallel orientation with respect to the plates, the orientation function is 0, while perpendicular orientation gives 1. In the isotropic case the value is 1/3.

The largest eigenvalue of the backbone presented in Fig. 6 displays the same behavior as that of R_e of the bottle-brush backbone presented in Fig. 2, again without a minimum. It can also be seen clearly that the largest principal axis of the backbone starts to orientate upon squeezing long before there is any deformation in the largest eigenvalue, a result which is in a good agreement with the observations by van Vliet and co-workers.[21,22] Figure 7 shows that the middle eigenvalue of the backbone starts to decrease at $\Delta Z=50$ having a minimum at $\Delta Z=20$ after which it increases towards its ultimate 2D value. The corresponding orientation of the principal axis has a maximum at around $\Delta Z=40$ after which it quickly decreases to 0. The smallest eigenvalue of the backbone, shown in Fig. 8, starts to decrease at $\Delta Z=30$ becoming 0 in the 2D limit. The orientation of the eigenvector at the same time increases monotonically towards the limiting value of 1.0, implying perpendicular orientation with respect to the confining plates.

While the eigenvalues and eigenvectors of the backbone behave in a rather conventional way, the behavior of the side chains differs from that of isolated free chains. The largest eigenvalue and the corresponding orientation of the eigenvector of the side chains, shown in Fig. 9, still behave as expected, showing a minimum of the eigenvalue analogous to R_e in Fig. 4. The middle eigenvalue in Fig. 10, on the other hand, behaves quite differently. Instead of a minimum, the eigenvalue has a maximum at about $\Delta Z=15$, after which it decreases until at $\Delta Z=5$ there is a minimum, and finally, at $\Delta Z=1$ the eigenvalue is again slightly larger. The orientation function of the middle eigenvector has a clear maximum at $\Delta Z=10$ and then decreases rapidly to 0 (parallel orientation) as the separation is further decreased. This kind of behavior appears to be the result of a competition between two opposing tendencies: As the separation between the plates ΔZ is decreased, isolated chains first reduce both their length and thickness (largest and middle eigenvalue), and after reaching a minimum increase them again.[21,22,24] However, due to the presence of other side chains, each side chain is confined into a more and more one-dimensional-(1D) like slab as all the side chains orientate parallel to the plates

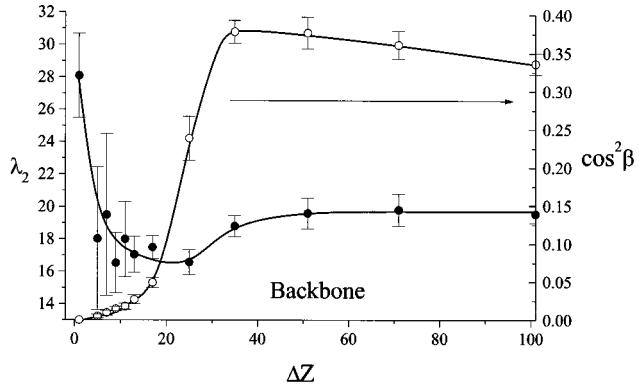

FIG. 7. The middle eigenvalue (●) λ_2 of the backbone and the orientation function of the corresponding eigenvector (○) $\cos^2\beta$ as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

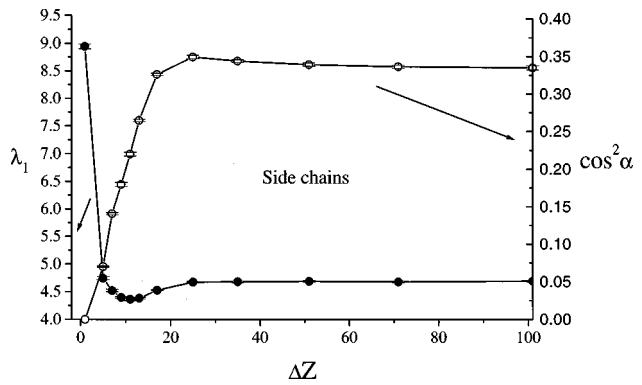

FIG. 9. The largest eigenvalue (●) λ_1 of the side chains and the orientation function of the corresponding eigenvector (○) $\cos^2\alpha$ as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

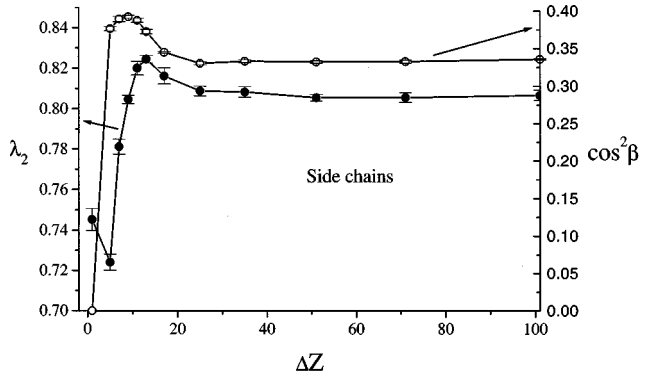

FIG. 10. The middle eigenvalue (●) λ_2 of the side chains and the orientation function of the corresponding eigenvector (○) $\cos^2\beta$ as a function of the separation between the confining plates ΔZ. The molecule consists of 100 backbone beads and 50 side chains, each 16 beads.

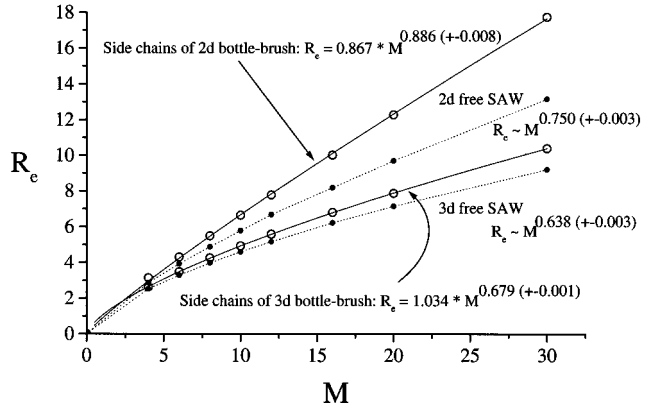

FIG. 12. Root-mean-square end-to-end distance R_e of the side chains of a bottle brush and of free self-avoiding walks (SAW) in 2D and 3D as a function of the side chain length M. The molecule consists of 100 backbone beads and 50 side chains.

during the squeezing. By comparing Figs. 9 and 8 we may also conclude that, in fact, the maximum of λ_2 is a consequence of the minimum of λ_1 which, therefore, seems to have a stronger tendency to obey its typical (free-chain) behavior. The smallest eigenvalue λ_3 has also a maximum, like the middle eigenvalue, however, at slightly smaller value of ΔZ and after that the value decreases towards the limiting value of 0. The orientation function increases monotonically and reaches 1.0 in the 2D limit.

B. Comparison between 2D and 3D molecular bottle brushes

After discussing the behavior of molecular bottle brushes with a fixed side chain length during squeezing between parallel plates, we now turn to a comparison between the pure 3D ($\Delta Z=\infty$) and pure 2D ($\Delta Z=1$) behavior as a function of the side chain length M. The behavior of the free 3D bottle brushes has been discussed already in some detail in our previous papers[13,14] and will only be briefly addressed here.

The whole idea of the extension of the bottle-brush backbone is based on the intramolecular excluded volume interactions between different side chains. To see whether these interactions are really effective in our structures, we consider Fig. 12, which shows the root-mean-square average of the end-to-end distance R_e of the side chains as a function of the side chain length M. Both in the 2D and 3D cases the data have only very small statistical errors, and the fitting of scaling functions leads to $R_e \sim M^{0.89}$ in 2D and $R_e \sim M^{0.68}$ in 3D. Of course, these scaling exponents should be considered with care since the chains are quite short. To check the finite-size effects, we also simulated short free linear (SAW) chains with the very same procedure as used for the side chains connected to the bottle-brush backbone. These results are also shown in Fig. 12. Clearly, in the 3D case the free chains do not obey the correct scaling ($R_e \sim M^{0.588}$) valid for very long self-avoiding chains, however, in 2D the scaling exponent is already identical to the predicted 0.75 even with these short chains. This is an important observations since it tells us that with the length of chains used, we may, in contrast to the 3D case, already be in or close to the final scaling regime for 2D. Of course, the excluded volume effect is effective in both cases because the side chains are clearly more extended than the corresponding free chains. Figure 13 shows the persistence length λ of the backbone as a function of the side chain length, as obtained by the afore-mentioned

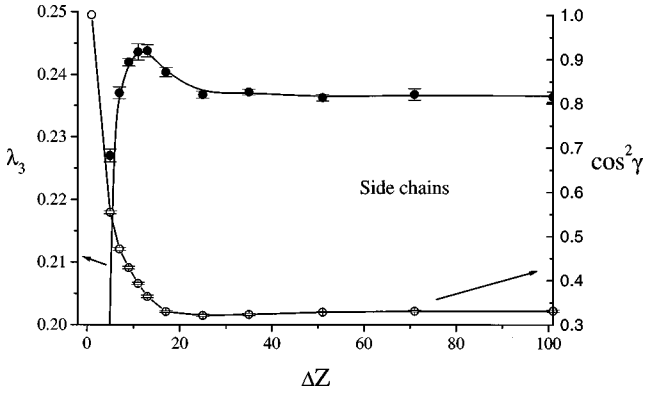

FIG. 11. The smallest eigenvalue (●) λ_3 of the side chains and the orientation function of the corresponding eigenvector (○) $\cos^2\gamma$ as a function of the separation between the confining plates ΔZ. The backbone consists of 100 beads and 50 side chains, each 16 beads.

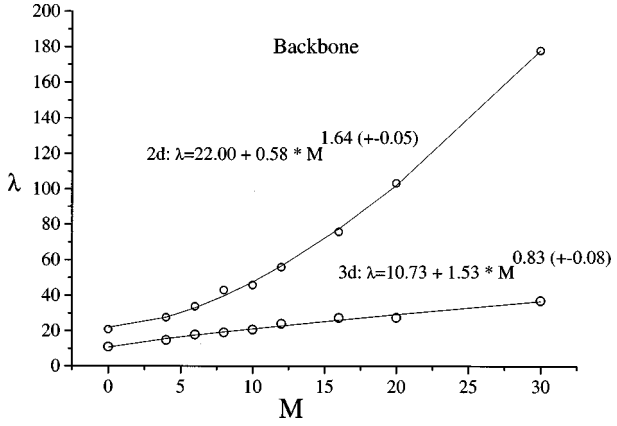

FIG. 13. Persistence length λ of the bottle-brush backbone in 2D and 3D as a function of the side chain length M. The molecule consists of 100 backbone beads and 50 side chains.

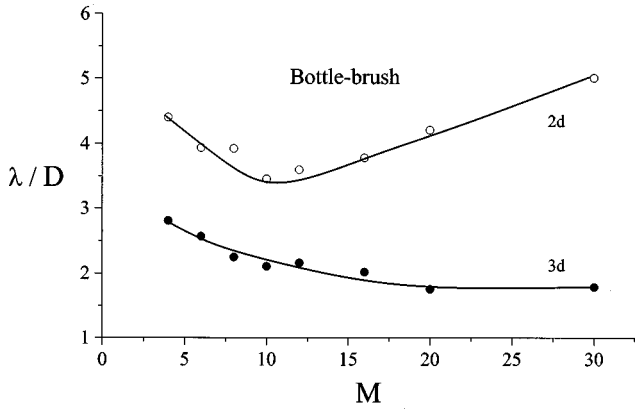

FIG. 14. The ratio of the persistence length λ and the bottle-brush diameter D in 2D and 3D as a function of the side chain length M. The molecule consists of 100 backbone beads and 50 side chains.

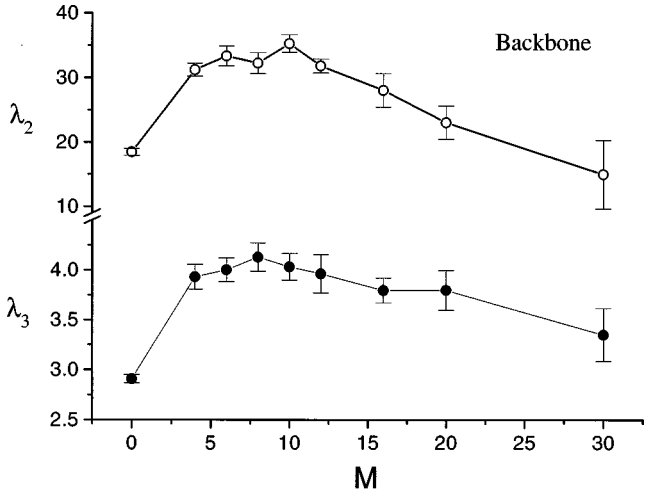

FIG. 15. The middle eigenvalue (○) λ_2 of the backbone of a 2D bottle brush and the smallest eigenvalue (●) λ_3 of the backbone of a 3D bottle brush as a function of the side chain length M. The molecule consists of 100 backbone beads and 50 side chains.

method using the bond-angle correlations. A monotonically increasing behavior of λ is obvious both in 2D and 3D, however, in 2D the increase of λ is much faster as a function of M. We have to emphasize again that the functional relations presented are supposed to be valid *in the studied regime* only.

The most interesting observation arises from the behavior of the ratio between the persistence length λ and the bottle-brush diameter D presented in Fig. 14 as a function of the side chain length M for $d=2$ and 3. As presented before, this ratio slightly decreases in 3D. However, in 2D it starts to increase for values of M larger than 10. Moreover, the ratio is always larger in 2D than in 3D. Though it is not possible to attach a precise exponent to the increase in 2D, the mere fact that λ/D increases as function of M lends credit to the prediction of Fredrickson.[9] Apparently, the strongly enhanced intramolecular excluded volume effect in 2D implies that the molecular bottle brushes approach their long chain scaling behavior for much smaller chain lengths (both side chain and backbone) than in the corresponding 3D case. If this statement is true, the implication is that λ/D may become an increasing function of M for $d=3$, but only for much longer chain lengths than those that have been computationally studied so far.[13,14]

Let us finally consider two other interesting quantities, namely, the middle eigenvalue of the backbone of a 2D bottle brush and the smallest eigenvalue of the backbone of a 3D bottle brush, both shown in Fig. 15. These quantities illustrate the slow crossover from 3D to 2D (respectively, from 2D to 1D) of the backbone of the 3D (respectively, 2D) bottle-brush backbone as the side chain length increases. However, it is an interesting observation that in both cases the backbone first increases its thickness (either middle or smallest eigenvalue) while the decrease begins only after a characteristic side chain length.

IV. CONCLUDING REMARKS

In this paper, we presented the results of a computational study on the equilibrium conformations of isolated molecular bottle brushes in a good solvent confined between two impenetrable parallel plates. All the interactions in the system were of the excluded volume type. The molecules were characterized in detail using parameters describing their size, shape, and orientation with respect to confining plates. We found both similarities and clear differences when comparing the behavior of molecular bottle brushes and simple linear chains.

The most interesting observations of this study can be summarized as follows. The ratio between the persistence length and the bottle-brush diameter, which is the essential parameter in relation to (nematic) lyotropic behavior, increases considerably as the molecules are squeezed between confining plates. Moreover, for a given side chain length, this ratio has a maximum for a characteristic separation between the plates. And even more interestingly, this ratio increases as a function of the side chain length in 2D, whereas it remains approximately constant in 3D for the chain lengths studied. Because in 2D the scaling regime, where the scaling approach is supposed to hold, is reached for much smaller chain lengths than in 3D, these results suggest that also in 3D the ratio λ/D may ultimately increase as a function of M. This then would imply that lyotropic behavior exclusively due to intramolecular excluded volume effects can be obtained for flexible polymers. The 2D results form a strong incentive to investigate much longer 3D molecular bottle brushes.

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